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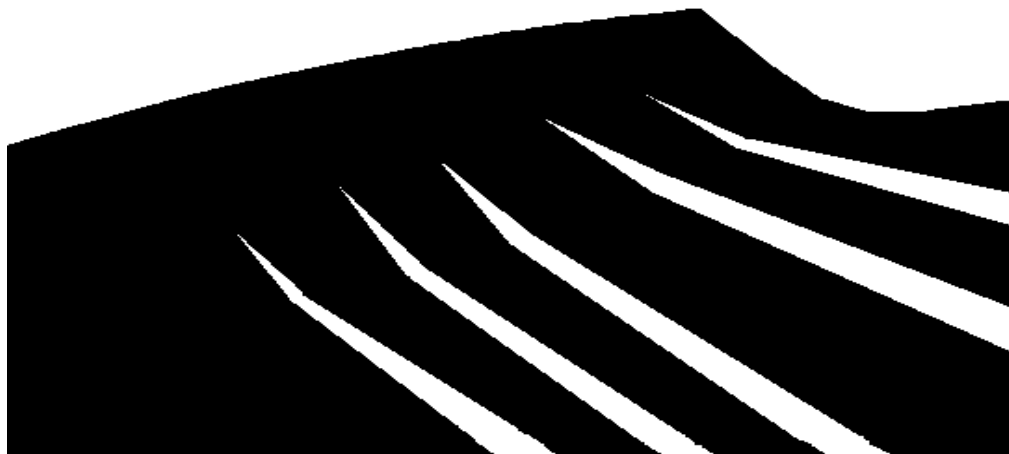
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LANL-CST-DP-92, R2

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## SAMPLE LEACHING TO EXTRACT SOLUBLE CHLORIDE AND BROMIDE

### *LOS ALAMOS QUALITY PROGRAM*



#### APPROVAL FOR RELEASE

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**Los Alamos**

Yucca Mountain Site

Characterization Project

## HISTORY OF REVISION

REVISION NO.	EFFECTIVE DATE	PAGES REVISED	REASON FOR CHANGE
R0	01/06/92	N/A	Initial procedure.
R1	04/28/93	All	Major rewrite.
R2	08/29/96	All	Major revision to expand the process to include the option of using isotopically enriched chlorine tracer as a carrier. Revision 1 (R1) of this procedure was previously identified as LANL-INC-DP-92.

**Los Alamos**Yucca Mountain Site  
Characterization Project

# **SAMPLE LEACHING TO EXTRACT SOLUBLE CHLORIDE AND BROMIDE**

## **1.0 PURPOSE**

This detailed technical procedure (DP) describes three sample leaching procedures used for extracting soluble chloride and bromide from soil and rock samples for the Yucca Mountain Site Characterization Project (YMP).

## **2.0 SCOPE**

This DP applies to all YMP personnel who conduct soil and rock sample leaching as part of the YMP's Water Movement Test task for Los Alamos National Laboratory (LANL).

## **3.0 REFERENCES**

LANL-YMP-QP-02.7	Personnel Training
LANL-YMP-QP-03.5	Documenting Scientific Investigations
LANL-YMP-QP-12.3	Control of Measuring and Test Equipment and Standards
LANL-INC-DP-88	Collection of Soil Samples for Analysis of Moisture Content, Bulk Density, Halides and Chlorine Isotopes
LANL-INC-DP-89	Procedure for Sieving Soil and Rock Samples
LANL-CST-DP-93	Step-Leaching Procedure for Extracting Soluble Chloride and Bromide
LANL-CST-DP-94	Using Ion Chromatography to Determine Chloride and Bromide Concentrations
LANL-CST-DP-95	Preparation of Samples for Chlorine-36 Analysis
LANL-CST-DP-97	Preparation of Carrier Solution for Chlorine-36 Samples
LANL-CST-DP-103	Identification, Storage, and Handling of Samples for the Water Movement Test

## **4.0 DEFINITIONS**

### **4.1 Samples**

Samples are geologic materials intended for laboratory studies or analyses as part of YMP site characterization investigations. Soil samples include any unconsolidated material above bedrock, i.e., the regolith, collected by the methods described in DP-88. Rock samples include, but are not limited to, surface samples, drill cores, drill cuttings, and samples from mining operations.

### **4.2 Leachate**

Leachate refers to the aqueous solution obtained by combining reagent water with a sample of soil or rock and allowing time for soluble constituents to dissolve into the water.

#### 4.3 Reagent Water

Reagent water is water that has been analytically purified to remove impurities so that the resistivity is greater than 17.5 megohms.

#### 4.4 Chloride Process Blank

The purpose of a chloride process blank is to test for the presence of chloride contamination in the materials used for processing samples for chloride and chlorine isotopic analyses. The chloride process blank consists of taking a volume of reagent water through the same processes, and using the same materials, as are used for actual samples, following this DP. Because the materials used in the leaching process should be chloride-free, the presence of chloride in the chloride process blank (detected following DP-94) may indicate a problem with chloride contamination.

#### 4.5 Carrier

Carrier is a chloride salt, prepared in solution pursuant to DP-97, that contains a negligible concentration of chlorine-36 ( $^{36}\text{Cl}$ ) relative to stable chlorine; ideally, the carrier should have a  $^{36}\text{Cl}/\text{Cl}$  ratio  $\# 5 \times 10^{-15}$ . Carrier may be added to a filtered leachate in order to increase the chloride mass to a level sufficient for isotopic analysis.

#### 4.6 Tracer

Tracer is a chloride salt that is a specific type of carrier in that it contains nearly pure chlorine-35 with only a negligible concentration of chlorine-37, in addition to a negligible concentration of  $^{36}\text{Cl}$ . Tracer may be added to a filtered leachate in order to increase the chloride mass to a level sufficient for isotopic analysis.

### 5.0 RESPONSIBILITIES

The following personnel are responsible for activities identified in section 6.0 of this procedure:

- Principal Investigator (PI)
- YMP Personnel (User)

### 6.0 PROCEDURE

The use of this procedure must be controlled as follows:

- If this procedure cannot be implemented as written, YMP personnel should notify appropriate supervision. If it is determined that a portion of the work cannot be accomplished as described in this DP, or would result in an

undesirable situation, that portion of the work will be stopped and not resumed until this procedure is modified, replaced by a new document, or current work practice is documented in accordance with QP-03.5, subsection 6.1.6.

- Employees may use copies of this procedure printed from the controlled document electronic file; however, employees are responsible for assuring that the correct revision of this procedure is used.
- When this procedure becomes obsolete or superseded, it must be destroyed or marked “superseded” to ensure that this document is not used to perform work.

## 6.1 Principle

Soil and rock samples included as part of the YMP Water Movement Test investigation need to be leached in order to extract soluble halides for subsequent analyses of chloride, bromide,  $^{36}\text{Cl}$ , and stable chlorine isotopes. Details of the leaching procedure described in this DP vary slightly depending upon whether subsequent analyses are only for total halides or for chlorine isotopes as well. Standardized leaching procedures ensure the consistency and integrity of analytical results.

## 6.2 Equipment and Hardware/Software

### 6.2.1 Equipment Malfunctions

Any equipment malfunction occurring during implementation of this procedure is likely to be readily detectable in the course of conducting work and hence is not expected to have a detrimental effect on the final results. The water purification system has a meter that indicates the resistivity of the purified water. This meter is checked each time water is drawn to verify that the resistivity is an acceptable value, i.e., at least 17.5 megohms. If a problem with any equipment arises which can be considered a potential source of error or uncertainty for the results, then it is addressed following section 6.7.

### 6.2.2 Safety Considerations

Good laboratory and scientific practices are used in the laboratory to protect against injury. Applicable LANL and/or LANL-contractor safety practices for conducting laboratory work are followed, as appropriate.

### 6.2.3 Special Handling

Care must be taken to minimize any potential for contamination of the carrier or tracer solution with  $^{36}\text{Cl}$  or Cl. Precautionary

measures are described in sections 6.2.4.2, 6.3.3, and 6.4.

#### 6.2.4 Equipment, Materials and Chemicals

Equipment, materials, and chemicals which may be needed to conduct soil and rock leaching are listed below. Required entries related to these items are listed in Attachment 2. Items equivalent to those listed below may be used provided they perform the same function with an acceptable level of performance as judged by the user or the PI. Not all of the following items may be needed for processing any given sample by this DP.

##### 6.2.4.1 Equipment

- water purification system capable of producing reagent water (e.g., Millipore Milli-Q Analytical Grade Deionizing Water Purification System, Model ZD20)
- analytical balance (e.g., Mettler Model AE 240 and Sartorius Model 3862 MP8-1)
- hot plate with temperature control up to 100EC or greater (e.g., Lindberg Hot Plate, Model 53015)
- centrifuge
- vacuum pump for filtration apparatus
- convection oven

All of the leaching procedures described in section 6.5 require the use of the analytical balance and water purification system, with use of the centrifuge being optional.

##### 6.2.4.2 Materials and Supplies

New labware is initially washed with detergent such as Alconox, rinsed with tap water, then rinsed three times with reagent water. Subsequent use requires rinsing three times with reagent water, unless excessive sample material or non-soluble compounds have contaminated a piece of labware, in which case the item is washed using the procedure for new labware. Just prior to use, each piece of labware is rinsed with a small volume of the solution it will contain. Filters used for filtering leachate are 0.45 micron cellulose nitrate filter membranes, which are flushed with reagent water prior to use and which are tested periodically for leachable chloride by preparing a process blank. A detailed list of materials and supplies is given in Attachment 1.

#### 6.2.4.3 Reagent chemicals

- reagent water
- high purity nitric acid ( $\text{HNO}_3$ )
- high purity ammonium hydroxide ( $\text{NH}_4\text{OH}$ )
- carrier or tracer solution, prepared pursuant to DP-97

### 6.3 Preparatory Verification

#### 6.3.1 Hold Points

The user contacts the PI to determine whether the sample needs to be sieved in accordance with DP-89 before being leached.

#### 6.3.2 Calibration

The analytical balance, which is used to weigh soil samples prior to leaching and carrier or tracer solution prior to its addition to a leachate, is controlled pursuant to QP-12.3.

#### 6.3.3 Environmental Conditions

Measures to minimize the potential for cross-contamination by particles or by sources of chloride and bromide other than that in the sample being analyzed are discussed in section 6.5. To monitor the adequacy of these measures, at least one chloride process blank is required to be processed as part of each sample suite.

### 6.4 Control of Samples

It is imperative that sample identification and control be sufficient to trace a sample and its derivatives from its original field location to the point of analysis and that the integrity of the sample be safeguarded during the entire analytical process. Consequently, users must be trained to DP-103 before they can work with samples analytically and they must also follow guidelines set forth in that document for sample management. Laboratory containers are labeled with the identifier of the sample that they are to hold, prior to that sample being transferred into them. This precaution will reduce the possibility of incorrect or ambiguous sample identification and cross-contamination.

### 6.5 Implementing Procedure

This section describes three procedures for leaching halides from soil and rock samples. The choice of method is determined by the user based both on the type of analysis to be performed and on the convenience of a particular method. Attachment 2 lists the information that is required to be documented in a laboratory notebook for work conducted under this DP.

Section 6.5.1 describes a batch extraction method to be used when the leachate is only to be analyzed for chloride and bromide concentrations, i.e., when sample size is relatively small (generally less than 1 kg).

Section 6.5.2 describes a batch extraction method to be used when the leachate is also to be analyzed for chlorine isotopic ratios, i.e., when sample size is relatively large (up to several kg).

Section 6.5.3 describes a column leaching method which can also be used when the leachate is to be analyzed for chlorine isotopic ratios. It is an alternative to the batch extraction method for large samples.

## 6.5.1 Batch Extraction Method for Halide Analyses

### 6.5.1.1 Sample Size Requirements

Leachable halides are extracted from soil or rock samples by mixing a weighed quantity of this material with a measured volume of reagent water, in an appropriately-sized container. For shallow soil samples which are likely to contain a high chloride content, 100 grams of soil, sieved as directed by the PI per section 6.3.1, is usually sufficient for determination of chloride and bromide content. For deep rock samples expected to be lower in chloride, 1-3 kg of rock material is probably sufficient for chloride and bromide determination. Again, this material may need to be processed according to section 6.3.1 prior to being leached. Sample masses are obtained using an analytical balance and recorded with a precision of 1% or better.

### 6.5.1.2 Leaching Procedure

The weighed air-dry sample is combined with a minimum volume of reagent water so as to maximize the sample: water ratio and hence the chloride concentration of the leachate (see note). The volume of water added is determined with a precision of 1% or better. After the sediment and water are combined, the mixture is stirred or swirled intermittently over a period of 48 hours, after which suspended solids in the sample are allowed to settle.

**NOTE:** The minimum volume of water which can be used must be sufficient to completely saturate the sample, with enough excess water to ensure that sufficient volume can be extracted for analysis (5 to 50 ml). An approximate proportion of 1:1 (on a mass basis) for sample: water generally is satisfactory in these regards.



#### 6.5.1.3 Extraction of Leachate for Analysis

A small volume of leachate (5 to 50 ml) is transferred to a clean sample container. This aliquot is analyzed for chloride and bromide following DP-94.

#### 6.5.1.4 Disposition of Leached Sample

If the solid sample or remaining leachate is to be saved, then the leachate is extracted from the soil or rock sample by decanting or by centrifugation. Generally, the only time that one would want to archive the leached solid material would be if step-leaching (DP-93) or particle-size analysis (DP-89) were to be conducted on it. If the leached solid is to be archived, then the residual solid sample material is dried, and stored in a sealed, labeled container for possible future use. The extracted leachate is stored in the refrigerator in a capped and labeled sample bottle for additional analyses. When the PI determines that there is no longer a need for the leached sample or the leachate, they can be discarded.

### 6.5.2 Batch Extraction Method for Chlorine Isotope Analyses

#### 6.5.2.1 Sample Size Requirements

Larger sample volumes are needed for determination of  $^{36}\text{Cl}$  than for chloride and bromide alone because isotopic analysis by the accelerator mass spectrometer requires a minimum of 1.5 mg chloride, with 4 mg chloride the preferred target amount. For shallow soil samples, approximately 1 kg of soil is needed; deep rock samples can require as much as 10 to 15 kg of material. These numbers are guidelines rather than absolutes. If the actual chloride content of a particular sample is known, e.g., by processing a small quantity following step 6.5.1, then the size requirements for leaching can be tailored to that sample. Sample masses can be obtained using either an analytical or mechanical beam balance and are recorded with a precision of 1% or better.

#### 6.5.2.2 Leaching Procedure

The weighed air-dry sample is combined with a minimum volume of reagent water so as to maximize the sample: water ratio and hence the chloride concentration of the leachate (see note). The volume of water added is determined with a precision of 1% or better. After the

sediment and water are combined, the mixture is stirred or swirled intermittently over a period of 48 hours, after which suspended solids in the sample are allowed to settle.

**NOTE:** The minimum volume of water which can be used must be sufficient to completely saturate the sample, with enough excess water to ensure that sufficient volume can be extracted for analysis and archiving (step 6.5.1.4). An approximate proportion of 1:1 (on a mass basis) for sample: water generally is satisfactory in these regards.

It is possible that the sample may need to be partitioned into several containers for leaching. After the sample and water are combined, the mixture is stirred or swirled intermittently over a period of 48 hours, after which the suspended solids in the sample are allowed to settle. After 48 or more hours, the leachate is extracted from the solid sample by suctioning, decanting, or centrifuging. If more than one container was used for the leaching of a single sample, then all leachates are combined into a single container at this point.

#### 6.5.2.3 Determination of Chloride, Bromide, and Adequacy of Sample Size

A small volume of leachate is transferred into a clean container and analyzed for chloride and bromide following DP-94. The total amount of chloride in the aqueous sample is roughly estimated using the measured chloride concentration and the leachate volume. If the total chloride is at least 4 mg, then an additional 50 ml or more of leachate is removed and stored in the refrigerator in a capped and labeled sample bottle as an archival sample for re-analysis if judged necessary. The user proceeds to step 6.5.2.5.

#### 6.5.2.4 Methods for Augmenting the Quantity of Chloride in a Sample

If the total chloride is significantly less than 4 mg, then the user may augment the recovered Cl by processing additional sample material; additional leachate is prepared following step 6.5.2.2, combined with the first leachate at the end of 6.5.2.2, and processed as a single sample starting with step 6.5.2.3. Alternatively, the user may decide that a known amount of carrier or tracer solution, prepared in accordance with DP-97, should be added to the leachate to increase the quantity of chloride. The archival sample described in step 6.5.2.3 is removed before the addition of

the carrier. The desired quantity of carrier solution is weighed and added to the leachate after the addition of nitric acid (step 6.5.2.5) and filtering (step 6.5.2.6).

#### 6.5.2.5 Addition of Nitric Acid

The leachate is acidified with high purity  $\text{HNO}_3$  acid (about 1 ml acid per liter of leachate) and any suspended material is allowed to settle overnight.

#### 6.5.2.6 Volume Determination

The leachate is filtered through a pre-rinsed 0.45 micron cellulose nitrate filter membrane. The volume or mass of the filtered leachate is measured to a precision of 10% or better. The volume is used in conjunction with the chloride analysis obtained previously in order to determine the total quantity of chloride in the leachate.

#### 6.5.2.7 Evaporation

It is difficult to recover good yields of chloride from highly dilute solutions (e.g.  $< 2 \text{ mg/L Cl}$ ). Consequently, dilute leachate volumes much greater than 1 liter are evaporated down to about 1 liter or less in volume. The pH of the sample is adjusted to 7 (using concentrated  $\text{NH}_4\text{OH}$ ) before the sample is heated in order to minimize the possible loss of chloride from the solution by volatilization of hydrogen chloride. The final volume of the evaporated leachate need not be determined.

#### 6.5.2.8 Preparation for Isotopic Analysis

The leachate is then processed into  $\text{AgCl}$  precipitate for  $^{36}\text{Cl}$  analysis following DP-95, or submitted as a solution to an outside laboratory for analysis of the stable chlorine isotope ratio.

#### 6.5.2.9 Disposition of Leached Sample

If the residual solid sample material is to be archived, then it is dried and stored in a sealed, labeled container for possible future use. If or when the PI determines that there is no longer a need for the leached sample or for the archived leachate, they can be discarded.

### 6.5.3 Column Leaching Method for Chlorine Isotope Analyses

#### 6.5.3.1 Sample Size Requirements

Column leaching is an alternative method for leaching kilogram quantities of soil or rock material. Volume requirements are the same as described in section 6.5.2.1.

#### 6.5.3.2 Initial Setup of Column

The column leaching method uses a simple device which allows water to flow slowly through the sample material, and theoretically should produce a smaller volume of leachate that is less turbid than that for the batch extraction method. A layer of glass wool is placed in the bottom of a wide-diameter glass tube, followed by a layer of reagent-grade quartz sand. Several kilograms of sample material, sieved if necessary according to section 6.3.1, are placed in the glass tube. The sample is then covered by an additional layer of quartz sand.

#### 6.5.3.3 Initial Saturation of Sample

The user may choose one of two ways to initially saturate the sample. First, a gravity-fed system, connected to the bottom of the sample cylinder, may be used to saturate the sample from below with reagent water. The inflow is stopped once outflow begins to occur above the upper layer of sand, i.e., flow is upward through the column. The pore volume is estimated at this point by noting the volume of water that was required to initially saturate the sample.

Alternatively, the user may choose to saturate the sample by adding reagent water to the sample in a large beaker and then transferring the slurry into the sample cylinder. This method minimizes the problem of air entrapment as the advancing wetting front saturates the column. The pore volume (needed for the next step) then must be estimated by the user. However, the accuracy of the porosity is not critical to the success of the procedure.

In either case, once the sample is saturated, it sits undisturbed for 48 or more hours.

#### 6.5.3.4 Leaching of Sample

After 48 or more hours, an additional 1-2 pore volumes of reagent water is slowly flushed through the system, and the entire volume of leachate is collected in a pre-cleaned container. The quartz sand placed on top of the sample in the column coarsely filters the leachate as it drains to the outlet.

#### 6.5.3.5 Determination of Chloride, Bromide, and Adequacy of Sample Size

A small volume of leachate is transferred into a clean container and analyzed for chloride and bromide following DP-94. The total amount of chloride in the aqueous sample is roughly estimated using the measured chloride concentration and the leachate volume. If the total chloride is at least 4 mg, then an additional 50 ml or more of leachate is removed and stored in the refrigerator in a capped and labeled sample bottle as an archival sample for re-analysis if judged necessary. The user proceeds to step 6.5.3.7.

#### 6.5.3.6 Methods for Augmenting the Quantity of Chloride in the Sample

If the total chloride is significantly less than 4 mg, then the user may augment the recovered Cl by processing additional sample material; the second leachate is prepared following steps 6.5.3.2 through 6.5.3.4, combined with the first leachate at the end of 6.5.3.4, and processed as a single sample starting with step 6.5.3.5. Alternatively, the user may decide that a known amount of carrier or tracer solution, prepared in accordance with DP-97, should be added to the leachate to increase the quantity of chloride. The archival sample described in step 6.5.3.5 is removed before the addition of the carrier or tracer. The desired quantity of carrier or tracer solution is weighed and added to the filtered leachate.

#### 6.5.3.7 Processing of the Leachate

Subsequent treatment of the leachate and disposition of the leached sample follow the procedures described in sections 6.5.2.5 through 6.5.2.9.

## 6.6 Data Acquisition and Reduction

Initial soil and water masses and volumes are generally determined with precisions of 1% or better, and volumes of recovered leachates with a precision of 10% or better. Masses and volumes determined for estimation purposes may have greater uncertainties. Attachment 2 lists the required data entries. Calculations using the data generated following this DP are verified by the PI before submission of the results to the Records Processing Center (RPC). The acceptability and precision of the data are also evaluated by the PI prior to submission of the results to the RPC, taking into account the precision of the instruments used as documented pursuant to QP-12.3.

## 6.7 Potential Sources of Error and Uncertainty

Careful labeling of containers reduces errors due to mislabeling. The possibility of sample contamination is reduced by working in a clean environment. The user is responsible for documenting deviations from this procedure in accordance with QP-03.5. If a problem arises which can be considered a potential source of error or uncertainty for the results, then it is also documented in the laboratory notebook or logbook in accordance with QP-03.5.

## 7.0 RECORDS

Records to be generated as a result of the proper execution of this DP are entries in laboratory notebooks or logbooks and in the Sample Inventory Logbook. These records are controlled by procedures QP-03.5 and DP-103. A checklist for laboratory notebook entries relevant to this DP is provided in Attachment 2.

## 8.0 ACCEPTANCE CRITERIA

The criteria that show that this procedure has been correctly implemented are the records identified in Section 7.0.

## 9.0 TRAINING

A prerequisite for this DP is to train to DP-103. This DP requires read-only training. Training of personnel to this DP is documented pursuant to QP-02.7.

## 10.0 ATTACHMENTS

Attachment 1: Detailed List of Materials and Supplies (1 page)  
Attachment 2: Checklist of Laboratory Notebook Entries (1 page)

## DETAILED LIST OF MATERIALS AND SUPPLIES

Materials and supplies for batch leaching (sections 6.5.1 and 6.5.2)

- glass beakers with covers (e.g., watch glasses, parafilm)
- large-volume (10 liters or more) stainless steel vessels
- volumetric pipets and pipet bulb
- volumetric flasks
- filtration apparatus
- pre-rinsed 0.45 micron cellulose nitrate membrane filters
- forceps
- vacuum flask
- tubing to connect vacuum flask to pump
- hot mitt or pot holder
- glass bottles (for archived leachates)

Materials and supplies for column leaching (section 6.5.3)

- large-diameter (e.g., 7-10 cm) glass tube, about 30 cm long, with a hose fitting on one end
- flexible tubing, with outer diameter to fit hose fitting on glass tube
- hose clamps
- glass funnel to serve as feed reservoir
- glass wool
- large ringstand with clamps, 1 for each setup
- pipet bulb and volumetric pipets
- volumetric flasks
- filtration apparatus
- pre-rinsed 0.45 micron cellulose nitrate membrane filters
- forceps
- vacuum flask for filtering
- tubing to connect vacuum flask to pump
- hot mitt or pot holder
- glass beakers
- glass bottles (for archived leachates)

## CHECKLIST OF LABORATORY NOTEBOOK ENTRIES

Initial descriptive information is entered in the laboratory notebook or logbook as required by QP-03.5 prior to starting a technical procedure and on a continuing basis as experimental and procedural changes dictate. These entries are:

- reference to this and any other relevant DPs, including revision number
- unique identifiers for any calibrated equipment used to conduct this DP
- manufacturer and lot number of any chemical reagents used in this DP

Additional information is entered into the laboratory notebook or logbook as relevant. These entries are:

- deviations from specified technical procedure (if any)
- acceptance or rejection of any data produced by a deviation from this DP
- problems (if any) which may pose a potential source of error or uncertainty for the results

In addition to general entries, several parameters need to be recorded in order to evaluate the resulting data. These entries are:

- sample processed, listed by its unique identifier
- air-dried mass of sample (1% precision or better)
- volume of reagent water added (1% precision or better)
- leaching method used (column or batch)
- leaching start date
- volume of extracted leachate (10% precision or better)
- volume of HNO<sub>3</sub> acid added (if any, 20% precision or better)
- mass and solution identifier for any carrier or tracer added (precision as stated in DP-97)